The Application of the Method of Moments to the General Concentration-Dependent Diffusion in One Dimension

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The method of moments is applied to problems of one-dimensional diffusion involving a general concentration-dependent diffusion coefficient. The general procedure of application is illustrated for the case in which a solute diffuses into a plane sheet of uniform thickness from a surrounding solution; for simplicity, it is assumed that both surfaces of the sheet attain a state of equilibrium with the surrounding solution instantaneously when the sheet is immersed in it. To simplify the mathematics only the zeroth and first moment equations are used in all the problems treated in this study. The general procedure is first applied to the case in which the diffusion coefficient is independent of concentration, in order to check the reliability of the method; excellent agreements are found with the exact solution in all respects examined, except for the behavior at sufficiently small values of time. The method is then applied to the diffusion coefficient varying linearly with concentration, again with a satisfactory agreement with the numerical and graphical solutions obtained by previous workers for this particular case. Approximate solutions are obtained, using the method of moments, for one-dimensional diffusion problems in a semi-infinite medium involving diffusion coefficients dependent both linearly and exponentially on concentration. They are compared with the numerical solutions of Crank and Henry, and it is found that for the diffusion coefficient of the former type the approximate solutions agree quite satisfactorily with the numerical ones up to as strong a concentration dependence as changing fifty-fold in the concentration range concerned, while for the diffusion coefficient of the latter type only poor agreement is obtained between the two solutions even for a relatively weak concentration dependence (about thirty-fold change).

1. INTRODUCTION

The method of moments is a simple means proposed in 1947 by Yamada[1] to obtain approximate solutions of differential equations appearing in the field of applied mechanics. It is particularly concerned with a hope of overcoming the difficulty arising from non-linearities of the fundamental equations in this field. The purpose of the present paper is to describe an application of this method to approximate solution of the diffusion equation in one dimension with a general concentration-dependent diffusion coefficient. In a previous paper[2], a brief account of the principle of this method and its application to a problem of one-dimensional

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diffusion with a coefficient dependent linearly on concentration has been given. A much more detailed treatment of the method and its applications to more numerous examples will be presented in this paper.

2. DIFFUSION INTO A PLANE SHEET

The principal character of the method of moments as applied to one-dimensional diffusion is best illustrated by considering the case in which a solute diffuses into a plane sheet of material from a surrounding solution. Suppose that an infinite sheet of uniform material of thickness $2X$ is placed in a solution and that the solute is allowed to diffuse into the sheet (Figure 1). In this case, the diffusion is obviously unidirectional and is governed by a Fick equation of the form:

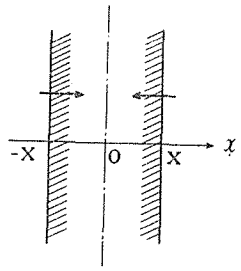

Fig. 1. Diffusion into a plane sheet from a solution.

$$\frac{\partial C}{\partial t}=\frac{\partial}{\partial x}\left[D(C)\frac{\partial C}{\partial x}\right], \tag{1}$$

where C is the concentration of the diffusing substance, $D(C)$ is the diffusion coefficient assumed here to be a function of C only, t is the time variable, and x is the space variable taken in the direction of diffusion. Initially the material is free of diffusing substance, so that the initial condition for C is

$$C(x,\ 0)=0 \quad (-X<x<X). \tag{2}$$

Assuming for simplicity that both surfaces of the sheet reach a state of equilibrium with the surrounding solution instantaneously when the sheet is immersed in the solution, the concentration of diffusing solute just within each surface should be maintained constant throughout the subsequent course of diffusion. If this surface concentration of diffusant is denoted by C_0, the boundary conditions are expressed as

$$C(X,\ t)=C_0 \quad (t>0), \tag{3}$$

$$C(-X,\ t)=C_0 \quad (t>0). \tag{4}$$

It follows at once that when the initial and boundary conditions are given by equations (2), (3), (4), the solution, $C(x,\ t)$, to equation (1) becomes symmetrical about the center of the sheet, $x=0$, so that we may replace these auxiliary conditions by

$$C(x,\ 0)=0 \quad (0\leqq x<X), \tag{5}$$

$$C(X,\ t)=C_0 \quad (t>0), \tag{6}$$

$$\frac{\partial C}{\partial x}=0 \qquad (x=0,\ t>0). \tag{7}$$

Our problem is then equivalent to finding a solution of equation (1) subject to these modified conditions in the range of x such that $0\leqq x<X$.

On introducing the dimensionless variables defined by

$$C/C_0=\phi,\quad x/X=z,\quad tD(0)/X^2=\tau,\quad D(C)/D(0)=F(\phi),$$

equation (1) and conditions (5) to (7) are written, respectively, as follows:

$$\frac{\partial\phi}{\partial\tau}=\frac{\partial}{\partial z}\left[F(\phi)\frac{\partial\phi}{\partial z}\right], \tag{8}$$

$$\phi(z,\ 0)=0 \quad (0\leqq z<1), \tag{9}$$

$$\phi(1,\ \tau)=1 \quad (\tau>0), \tag{10}$$

$$\frac{\partial\phi}{\partial z}=0 \qquad (z=0,\ \tau>0). \tag{11}$$

Formal solutions for this set of equations are not yet known, except for the case of a constant diffusion coefficient, i.e., $F(\phi)\equiv 1$. So we shall here attempt to solve this system approximately by making use of the method of moments. For the time being we can proceeed without making any restriction as to the form of the reduced diffusion coefficient, $F(\phi)$.

In applying the method of moments to any given problem, it is first necessary to decide how many moment-equations we choose for the purpose of the calculation concerned. As was clarified by Yamada[1], the simplest case in which only the zeroth moment-equation is taken leads to the well-known Kármán-Pohlhausen method for obtaining approximate solutions of the laminar boundary layer equations. Recalling that the method of moments has realized many satisfactory results in the field of hydrodynamics even in this simplest case, it is expected that better results would be obtained if we proceed to the next step of approximation by taking the moment-equations up to the first one. On the basis of this prediction we shall, in this paper, attempt all calculations using the zeroth and first moment-equations only. These, when applied to equation (8), take, respectively, the forms:

$$\int_0^1\left\{\frac{\partial\phi}{\partial\tau}-\frac{\partial}{\partial z}\left[F(\phi)\frac{\partial\phi}{\partial z}\right]\right\}dz=0, \tag{12}$$

and

$$\int_0^1\left\{\frac{\partial\phi}{\partial z}-\frac{\partial}{\partial z}\left[F(\phi)\frac{\partial\phi}{\partial z}\right]\right\}zdz=0. \tag{13}$$

The problem to be solved is now reduced to finding the expression of $\phi(z,\ \tau)$ satisfying these two moment-equations together with conditions (9) to (11).

It is usually found in practice that in the early stages of diffusion into a plane

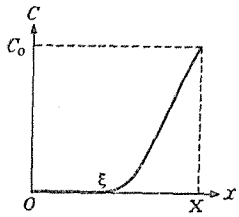

Fig. 2 Schematic diagram of the concentration distribution in a plane sheet.

sheet, when the concentration has not become appreciable at the center of the sheet, the concentration distribution in the sheet presents a general character as shown schematically in Figure 2. It is characterized by a very flat portion extending over a range from the center toward the surface of the sheet. Initially, when the sheet was immersed in the solution, this flat portion extended over the entire range in the sheet, since the sheet was initially free from diffusing solute. As the time goes on, the solute diffuses into the sheet and makes up a concentration distribution as illustrated in the figure. Concurrently, the flat portion is eroded step by step from its outside, and ultimately disappears when the solute has just arrived at the center of the sheet. Strictly speaking from the theoretical point of view, such flat portion cannot be realized for $t>0$, because at just the next instant when the sheet was immersed in the solution some particle of diffusant should already be found everywhere in the sheet, thus resulting in a non-zero concentration distribution throughout the sheet. Nevertheless, it is useful for practical purpose to assume a physical pitcure as described above in place of the theoretically rigorous diffusion behavior, because, as will be shown, by virtue of this model our mathematical analysis for the early stage of diffusion can be simplified considerably without significant loss of correctness.

Now, according to the picture described above, the concentration distribution curve in the interval of time until the diffusant amount becomes appreciable at the center of the sheet may be approximated by a curved portion followed by a horizontal part coinciding with the x-axis. This approximation is equivalent to replacing a region over which the concentration is almost zero by a region where the concentration is completely zero. Denote by ξ the point at which the curved portion is continued to the flat portion. The quantity ξ is obviously a function of time which starts at $t=0$ with $\xi=X$, advances toward the center, and reaches there after a certain interval of time, say t_*.

We shall first calculate the solution applicable for this interval of time based on the approximation presented above.

Denote the value of z corresponding to ξ by Z. With the properties in mind that no source of diffusing substance exists in the sheet and, in addition, that diffusant does not react with the medium, we assume in the curved portion, i.e., $Z\leqq$

$z \leqq 1$, a cubic equation of the form:

$$\psi(z, \tau)=B(\tau)[z-Z(\tau)]^2+C(\tau)[z-Z(\tau)]^3, \tag{14}$$

where $B(\tau)$, $C(\tau)$, and $Z(\tau)$ are unknown functions of τ to be determined from the system of equations consisting of the zeroth and first moment-equations. For the equation of ψ in the flat portion, i.e., $0 \leqq z \leqq Z$, we may simply assume

$$\psi(z, \tau)=0 \quad (0 \leqq z \leqq Z). \tag{15}$$

We note first that the equations assumed here are constructed so as to fulfill the condition (11) automatically. It is also known that the initial condition (9) may be replaced by

$$Z(0)=1. \tag{16}$$

It is readily shown that when this condition is satisfied, the concentration distribution at $\tau=0$ is represented by equation (15) over the whole range of z in the sheet and, therefore, satisfies the initial condition (9).

Introducing equation (14) into the condition (10), and putting

$$B(1-Z)^2=U, \quad C(1-Z)^3=V, \tag{17}$$

we obtain a relation between U and V as

$$U+V=1. \tag{18}$$

Inserting equations (14) and (15) into the zeroth moment-equation (12), integrating, and taking condition (10) into account, we obtain

$$\frac{d}{d\tau}\left[(1-Z)\left(\frac{U}{3}+\frac{V}{4}\right)\right]=\frac{F(1)(2U+3V)}{1-Z}, \tag{19}$$

which, on eliminating V by equation (18), reduces to

$$\frac{d}{d\tau}\left[(1-Z)\left(1+\frac{U}{3}\right)\right]=\frac{12F(1)}{1-Z}\left(1-\frac{U}{3}\right). \tag{20}$$

In an analogous way we obtain from the first moment-equation an equation of the from:

$$\frac{d}{d\tau}\left[(1-Z)^2\left(1+\frac{2U}{3}\right)\right]=20\,G(1) \tag{21}$$

where $G(\psi)$ denotes

$$G(\psi)=\int_0^{\psi}F(\psi)d\psi. \tag{22}$$

The quantity $G(1)$ gives an average of the given diffusion coefficient-concentration relationship, and is equivalent to the quantity D_1 used by Crank and Henry[3] in one of their series of papers on the diffusion in media with variable properties. Equation (21) can be integrated to give

$$\varphi^2\left(\frac{3}{2}+U\right)=a\tau\,, \tag{23}$$

where

$$a=30\,G(1),\quad \varphi=1-Z. \tag{24}$$

The integration constant has been determined in terms of condition (16). Introduction of equation (23) into equation (20) leads to the following differential equation of the first order:

$$\frac{d}{d\tau}\left(\frac{\varphi}{2}+\frac{a\tau}{3\varphi}\right)=\frac{12F(1)}{\varphi}\left(\frac{3}{2}-\frac{a\tau}{3\varphi^2}\right). \tag{25}$$

The solution of this equation satisfying the condition that $\varphi(0)=0$ (which is also derived from condition (16)) is given by

$$\varphi=(\tau/\beta)^{1/2}, \tag{26}$$

where β is a constant determined from the following quadratic equation:

$$24\,a\,F(1)\beta^2+[a-108\,F(1)]\beta+\frac{3}{2}=0\,. \tag{27}$$

In order that the solution (26) may have any physical meaning, β must be a positive quantity. Furthermore, if there exist in equation (27) two positive roots, the question arises which positive root is to be taken. As was pointed out by Yamada, similar questions are often encountered in dealing with problems in applied mechanics by means of the method of moments. Although an analytic procedure by which to resolve these questions has been suggested and actually used by Yamada, it is too cumbersome to be put into practice. Despite this difficulty, the decision which root is appropriate for a particular problem concerned can, in general, be obtained without considerable ambiguity by considering a relevant limiting case for which the exact or a suitable approximate solution of the problem may be obtained. In all the practical examples dealt with in this paper, the correct choice of β is made possible by considering the case of a constant diffusion coefficient.

Now, if we denote by τ_* the value of τ at which Z, i.e., the front line of the concentration distribution, reaches the center of the sheet, $\varphi=1$ at $\tau=\tau_*$, so that we have from equation (26)

$$\beta=\tau_*. \tag{28}$$

This relation provides a physical meaning of the constant β, i.e., β gives a measure for the interval of time until the concentration at the center of the sheet can no longer be regarded as effectively zero. Inserting equation (26) into equation (23) leads to the expression for U:

$$U=a\beta-\frac{3}{2}\,. \tag{29}$$

The expression for V then is found to be

$$V=-\alpha\beta+\frac{5}{2}. \tag{30}$$

It is found that both U and V are constant quantities. The expression for Z is obviously given by

$$Z=1-(\tau/\beta)^{1/2}. \tag{31}$$

Substituting all of these into equation (14) with the substitutions (17) in mind, we arrive at the result that

$$\psi(z,\ \tau)=\left(\alpha\beta-\frac{3}{2}\right)\left(\frac{\tau}{\beta}\right)\left(z-1+\sqrt{\frac{\tau}{\beta}}\right)^2-\left(\alpha\beta-\frac{5}{2}\right)\left(\frac{\tau}{\beta}\right)^{3/2}\left(z-1+\sqrt{\frac{\beta}{\tau}}\right)^3$$
$$\left(1-\sqrt{\frac{\tau}{\beta}}\leqq z\leqq 1\right), \tag{32}$$

$$\psi(z,\ \tau)=0\quad\left(0\leqq z\leqq 1-\sqrt{\frac{\tau}{\beta}}\right). \tag{33}$$

From equation (32) the concentration distribution at the time when the diffusant has just arrived at the center of the sheet can be obtained, giving

$$\psi(z,\ \tau_*)=\left(\alpha\beta-\frac{3}{2}\right)z^2-\left(\alpha\beta-\frac{5}{2}\right)z^3\quad(0\leqq z\leqq 1). \tag{34}$$

Our next problem is to derive an approximate solution which holds for later time when the concentration has become appreciable at the center of the sheet. Such a solution must naturally be a smooth continuation of the solution obtained above for $\tau\leqq\tau_*$. With this requirement as well as condition (11) in mind, we assume for ψ in the later stage of diffusion a similar cubic equation in z of the form:

$$\psi(z,\ \tau)=A(\tau)+B(\tau)z^2+C(\tau)z^3\quad(0\leqq z\leqq 1), \tag{35}$$

where $A(\tau)$, $B(\tau)$, and $C(\tau)$ are unknown functions of τ to be determined, but, of course, not the same as the analogous quantities defined previously. It is at once noted that the first term, $A(\tau)$, in equation (35) represents the concentration at the center of the sheet. It is also noted that equation (35) is assumed so as to satisfy the condition (11) automatically.

Condition (10), when inserted in equation (35), gives a relation among A, B and C:

$$A+B+C=1. \tag{36}$$

The zeroth and first moment-equations in this case lead, respectively, to the following equations:

$$\frac{d}{d\tau}\left(A+\frac{B}{3}+\frac{C}{4}\right)=F(1)(2B+3C), \tag{37}$$

$$\frac{d}{d\tau}\left(\frac{A}{2}+\frac{B}{12}+\frac{C}{20}\right)=G(1)-G(A). \tag{38}$$

Eliminating C by use of the relation (33), and putting

$$\frac{dA}{d\tau}=\Phi, \tag{39}$$

we have from equations (37) and (38)

$$\frac{3}{4}\Phi+\frac{1}{12}\Phi\frac{dB}{dA}=F(1)(3-B-3A), \tag{40}$$

$$\frac{9}{20}\Phi+\frac{1}{30}\Phi\frac{dB}{dA}=G(1)-G(A), \tag{41}$$

If we eliminate B from these two equations by taking an obvious relation $dG(A)/dA=F(A)$ into account, there results

$$\frac{d\Phi}{dA}=-28F(1)-\frac{20}{3}F(A)-\frac{80F(1)[G(A)-G(1)]}{\Phi}. \tag{42}$$

This equation is reduced to a more tractable form as

$$\Psi\frac{d\Psi}{d\varphi}=\frac{49}{5}[r(\varphi)\Psi-q(\varphi)], \tag{43}$$

by introducing the following new variables:

$$\varphi=1-A, \tag{44}$$

$$\Psi=\frac{7}{20F(1)}\Phi, \tag{45}$$

$$r(\varphi)=1+\frac{5}{21}\left[\frac{F(A)}{F(1)}\right]_{A\to\varphi}, \tag{46}$$

$$q(\varphi)=\int_0^{\varphi}\left[\frac{F(A)}{F(1)}\right]_{A-\varphi}d\varphi. \tag{47}$$

Since the solution given by equation (35) must coincide with the solution (34) at $\tau=\tau_*$ over the whole range of z from the center to the surface of the sheet, it is required that

$$A(\tau_*)=0, \tag{48}$$

$$B(\tau_*)=\alpha\beta-\frac{3}{2}, \tag{49}$$

$$C(\tau_*)=-\alpha\beta+\frac{5}{2}. \tag{50}$$

Among these conditions the last one is automatically satisfied when the first two are fulfilled, by virtue of condition (36). Eliminating the term $\Phi\ dB/dA$ from equations (40) and (41), and expressing the resultant equation in terms of the variables newly introduced above, we obtain

$$B=\frac{15}{14}\Psi(\varphi)+3\varphi-\frac{5}{2}q(\varphi). \tag{51}$$

From equations (44), (48) and (49) it follows that $B=\alpha\beta-\frac{3}{2}$ when $\varphi=1$, and so we have from equation (51)

$$\Psi(1)=\frac{14}{15}\left[\alpha\beta-\frac{9}{2}+\frac{5}{2}q(1)\right]. \tag{52}$$

For any given concentration-dependent diffusion coefficient the quantities $r(\varphi)$ and $q(\varphi)$ may be evaluated, formally or numerically, as functions of φ, where the range of φ to be treated is such that $0<\varphi\leqq 1$. This condition follows immediately if we note that A, the concentration at the center of the sheet, is zero at $\tau=\tau_*$ and tends monotonically to an equilibrium value 1, as the time goes to infinity. Obviously, $\varphi=1$ corresponds to $\tau=\tau_*$ and $\varphi\to 0$ to $\tau\to\infty$. Thus, it is found that equation (52) gives the initial condition with which the differential equation (43) for Ψ should be integrated over the range of φ from 1 to 0. Unfortunately, this type of differential equation of the first order cannot be integrated analytically, except for only one special case which, as shown in section 3, corresponds to a constant diffusion coefficient. Consequently, when the diffusion coefficient is dependent on concentration we must resort to an appropriate method of numerical integration.

Once the solution of equation (43) is known, we obtain $\Phi(A)$ from equation (45). On the other hand, integrating equation (39) and using the condition that A must vanish at $\tau=\tau_*$, there results a relation:

$$\tau=\tau_*+\int_0^A\frac{dA}{\Phi(A)}. \tag{53}$$

Inserting the solution $\Phi(A)$ obtained above, and carrying out the integration, the required relation between A and τ is determined; it provides a picture of the physical process in which the concentration on the central plane of the sheet changes with time.

Once the A-τ relation is determined, the φ-τ relation follows straightforwardly, which in turn gives B as a function of τ when it is inserted in equation (51) together with the Ψ-φ relation obtained. Finally, using these results for $A(\tau)$ and $B(\tau)$, the C-τ relation is obtained from equation (36). In this way, all the unknown functions of τ in the right-hand side of equation (35) are uniquely determined.

The total amount of diffusant, M_t, absorbed by the sheet at time t is given by

$$M_t=2S\int_0^X C(x,\ t)\ dx, \tag{54}$$

where S is the surface area of the sheet concerned. Equation (54) may be written

$$M_t=2SXC_0\int_0^t\psi(z,\ \tau)\ dz. \tag{55}$$

For t in which the concentration is regarded as effectively zero at the center or the sheet, i.e., $t<t_*$, ψ is given by equations (32) and (33), and so the expression of M_t in this range of time is shown to be given by

$$M_t=2SXC_0\left(\frac{1}{8\sqrt{\beta}}+\frac{\alpha\sqrt{\beta}}{12}\right)\sqrt{\tau}. \tag{56}$$

For t greater than t_* it is easily shown that

$$M_t=2SXC_0\left\{1-\frac{2}{3}B(\tau)-\frac{3}{4}C(\tau)\right\}. \tag{57}$$

From equation (56) it is found that M_t in the early stage of diffusion into a plane sheet is proportional to the square root of time, irrespective of the form of a particular diffusion coefficient-concentration relationship concerned. This fact is often confirmed experimentally with considerable certainty ; it is used to validate the diffusion to be Fickian.

3. EXAMPLES

In this section the general analytic procedure developed above is applied to several practical cases of the diffusion coefficient-concentration relationship, in the hope of checking the validity of the present approximate method of solution as applied to concentration-dependent diffusion.

A. The case in which D is constant

First the method is applied to the simplest case in which D is not dependent on concentration, i.e., $D=$constant. Since for this case the exact solution of the problem is well-known, it is possible to check the validity of the method with a best certainty. The exact solution is given by

$$\psi(z,\ \tau)=1-2\sum_{n=0}^{\infty}\frac{(-1)^n}{\alpha_n}e^{-\alpha_n^2\tau}\cos\alpha_n z, \tag{58}$$

where

$$\alpha_n=\left(\frac{2n+1}{2}\right)\pi. \tag{59}$$

When D is constant, $F(\psi)=1$, and so equation (27) becomes

$$720\,\beta^2-78\,\beta+\frac{3}{2}=0, \tag{60}$$

which yields two positive roots such that

$$\beta=\frac{1}{12},\quad \frac{1}{40}. \tag{61}$$

Although we shall not present here the details of the comparison, it can be shown

that the larger root, i.e., $\beta=1/12$, leads to a better approximation to the exact solution than does the smaller root. For this reason we shall in what follows take the value of β to be 1/12.

With $\beta=1/12$, we obtain from equations (32) and (33)

$$\psi(z,\ \tau)=\frac{1}{12}(z-1+2\sqrt{3\tau})^2 \quad (1-2\sqrt{3\tau}\leqq z\leqq 1), \tag{62}$$

$$\psi(z,\ \tau)=0 \quad (0\leqq z\leqq 1-2\sqrt{3\tau}), \tag{63}$$

which gives the concentration distribution in the time interval $\tau\leqq\tau_*$. The value of τ_* is given as

$$\tau_*=\frac{1}{12}. \tag{64}$$

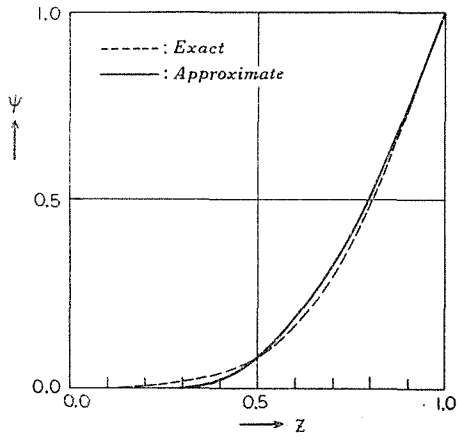

Fig. 3. Concentration distribution at $\tau=$ 0.04 for the case in which D is independent of C.

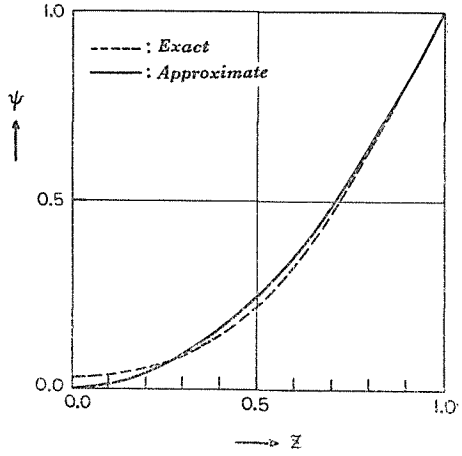

Fig. 4. Concentration distribution at $\tau=$ 0.0833 for the case in which D is independent of C.

Figures 3 and 4 show the concentration distribution curves at $\tau=0.04$ and 0.08333 ($=1/12$), respectively, computed from both approximate (solid line) and exact (dashed line) solutions. Although the agreement is fairly good at either τ, there is observed a discrepancy of about 5% in the largest. Therefore it cannot be claimed that the degree of approximation of the present solution is so good, at least in the early stage of diffusion before the concentration becomes appreciable at the center of the sheet. However, this degree of approximation may be sufficient for most practical purposes.

When $F=1$, it is shown that the equations for $r(\varphi)$ and $q(\varphi)$ become

$$r(\varphi)=\frac{26}{21}, \quad q(\varphi)=\varphi.$$

Hence, equation (43) takes the form:

$$\frac{d\Psi}{d\varphi}=\frac{49}{5}\left(\frac{26}{21}-\frac{\varphi}{\Psi}\right), \tag{65}$$

which can be integrated formally to give a general solution of the form:

$$\varphi^{p_2-p_1}=K\frac{(u-p_1)^{p_1}}{(u-p_2)^{p_2}}, \tag{66}$$

where K is an integration constant, u is a new variable defined by

$$u=\frac{\Psi}{\varphi}, \tag{67}$$

and p_1 and p_2 are the roots of a quadratic equation:

$$p^2-\frac{182}{15}p+\frac{49}{5}=0. \tag{68}$$

It can be shown that these roots are positive and give the values:

$$p_1=0.87007, \quad p_2=11.2633. \tag{69}$$

The initial condition for $\Psi(\varphi)$ as given by equation (52) now yields

$$\Psi(1)=7/15, \tag{70}$$

so that

$$u=7/15 \quad \text{at} \quad \varphi=1. \tag{71}$$

This condition makes the determination of the integration constant K possible, and leads to the required solution as follows:

$$\varphi=\left(\left(\frac{p_1-u}{p_1-\frac{7}{15}}\right)^{p_1}\left(\frac{p_2-\frac{7}{15}}{p_2-u}\right)^{p_2}\right)^{\frac{1}{p_2-p_1}}. \tag{72}$$

If we next rewrite equation (53) in the form

$$\tau=\tau_*+\frac{7}{20F(1)}\int_{\varphi}^{1}\frac{1}{u}\frac{d\varphi}{\varphi}, \tag{73}$$

and substitute in this a relation

$$d\varphi/\varphi=-udu/(p_1-u)(p_2-u),$$

which can easily be derived from equation (72), there results an equation:

$$\tau-\tau_*=-\frac{7}{20(p_2-p_1)}\ln\left(\frac{p_1-u}{p_1-\frac{7}{15}}\right)\left(\frac{p_2-\frac{7}{15}}{p_2-u}\right). \tag{74}$$

From equations (72) and (74) the required relation between φ and τ may be calculated with u as an intermediate parameter. However, it can be shown that it is possible to eliminate u from these two equations to obtain an explicit equation

for φ in terms of τ. The result reads

$$\varphi=\frac{1}{p_2-p_1}\left\{\left(p_2-\frac{7}{15}\right)e^{-(20/7)p_1(\tau-\tau_*)}-\left(p_1-\frac{7}{15}\right)e^{-(20/7)p_2(\tau-\tau_*)}\right\}, \quad (75)$$

which may actually be written

$$\varphi=1.278\ e^{-2.486\tau}-0.5671\ e^{-32.18\tau}. \quad (76)$$

Thus,

$$A(\tau)=1-1.278\ e^{-2.486\tau}+0.5671\ e^{-32.18\tau}. \quad (77)$$

Once the expression of $A(\tau)$ is obtained in this way, the corresponding expressions for $B(\tau)$ and $C(\tau)$ can be derived easily according to the general procedure presented in section 2. In this place, only the results are shown, which are, respectively,

$$B(\tau)=1.830\ e^{-2.486\tau}-7.126\ e^{-32.18\tau} \quad (78)$$

and

$$C(\tau)=-0.5524\ e^{-2.486\tau}+6.559\ e^{-32.18\tau}. \quad (79)$$

Thus, we have

$$\psi(z,\ \tau)=1-(1.278-1.830\ z^2+0.5524\ z^3)\ e^{-2.486\tau}+(0.5671-7.126\ z^2+6.559\ z^3)\ e^{-32.18\tau}, \quad (80)$$

which gives the concentration distribution for later times when the concentration at the sheet becomes appreciable and increases toward the final equilibrium value.

Comparison of the above approximate solution for $\tau>\tau_*$ with the coresponding exact solution is shown below.

First, we make this comparsion with respect to the ψ value at the center of the sheet. The exact value, being denoted by $(\psi_c)_e$, is obtained by putting $z=0$ in equation (58), i.e.,

$$(\psi_c)_e=1-2\sum_{n=0}^{\infty}\frac{(-1)^n}{a_n}e^{-a_n^2\tau}\quad(\tau>0). \quad (81)$$

On the other hand, our approximate value, being denoted by $(\psi_c)_a$, is directly given by equation (77), i.e.,

$$(\psi_c)_a=1-1.278\ e^{-2.486\tau}+0.5671\ e^{-32.18\tau}. \quad (82)$$

It should be noted that this approximate equation is applicable only for $\tau>\tau_*=1/12$. For $\tau<\tau_*$ this must be continued with

$$(\psi_c)_a=0. \quad (83)$$

Figure 5 shows the comparison between $(\psi_c)_e$ and $(\psi_c)_a$, from which one can see that, except for a region where τ is smaller than 0.15, the agreement of both solutions is almost perfect.

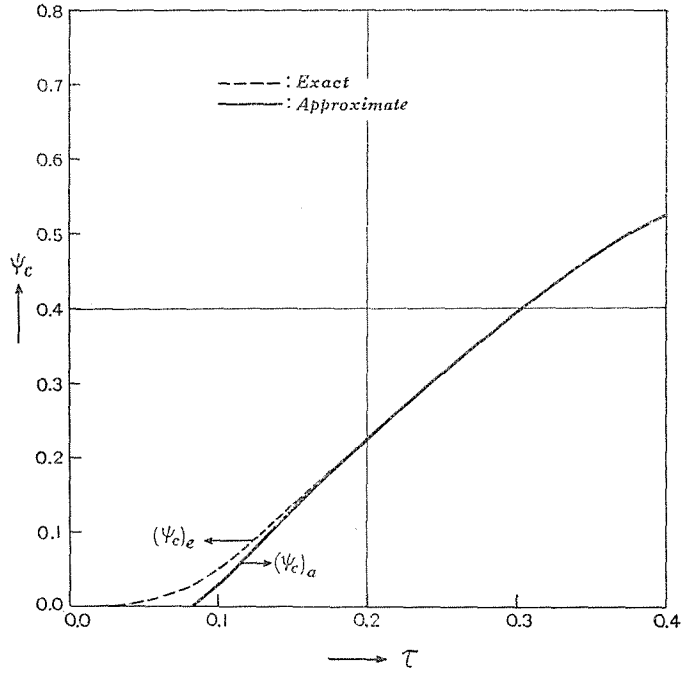

Fig. 5. Comparison of the concentration at the center of the sheet where D is independent of C.

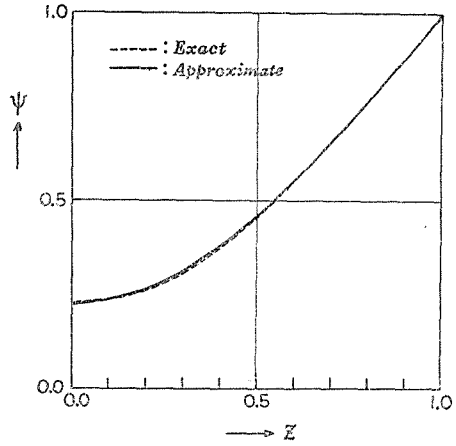

Fig. 6. Comparison of the concentration at $\tau=0.20$ for the case in which D is independent of C.

Comparsion of the ϕ–z curves computed from both approximate and exact solutions at a particular value of τ (here 0.20) is shown in Figure 6. The agreement of the two curves is also satisfactory over the whole range of z. Although the results are not reproduced here, it was found that the degree of agreement between the approximate solution and the exact one becomes increasingly better as τ increases.

Finally, we calculate the sorption-time curve. Since the concentration distribu-

tion in the sheet tends uniform when the time increases indefinitely, the final value, M_∞, of M_t when $t \to \infty$ is given by

$$M_\infty = 2SXC_0. \tag{84}$$

Thus, equations (56) and (57) are, respectively, put in the forms:

$$\frac{M_t}{M_\infty} = \left(\frac{1}{8\sqrt{\beta}} + \frac{\alpha\sqrt{\beta}}{12}\right)\sqrt{\tau} \quad (\tau > \tau_*) \tag{85}$$

and

$$\frac{M_t}{M_\infty} = 1 - \frac{2}{3}B(\tau) - \frac{3}{4}C(\tau) \quad (\tau > \tau_*). \tag{86}$$

Substituting in these equations from the relevant equations derived above, it follows that

$$\frac{M_t}{M_\infty} = \frac{2}{\sqrt{3}}\sqrt{\tau} \quad \left(\tau < \frac{1}{12}\right), \tag{87}$$

$$\frac{M_t}{M_\infty} = 1 - 0.806\, e^{-2.486\tau} - 0.164\, e^{-32.18\tau} \quad \left(\tau > \frac{1}{12}\right). \tag{88}$$

The corresponding exact equation for M_t/M_∞ is

$$\frac{M_t}{M_\infty} = 1 - 2\sum_{n=1}^{\infty} \frac{e^{-\alpha_n^2 \tau}}{\alpha_n^2}. \tag{89}$$

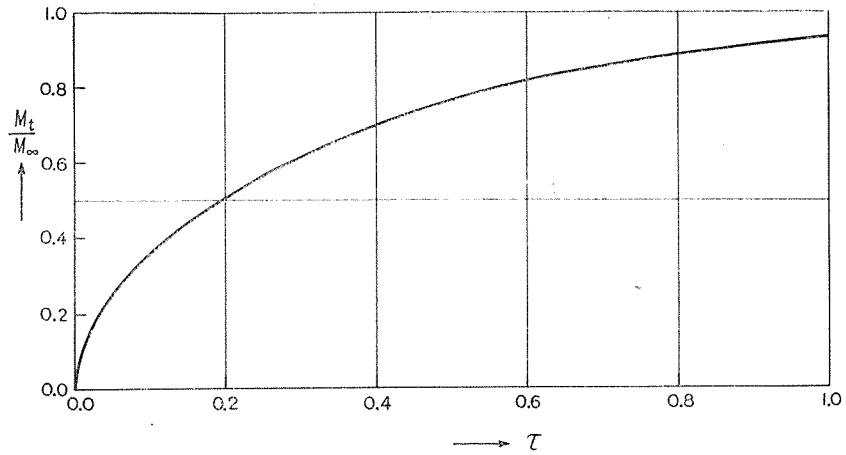

Fig. 7. Sorption-time curve for the case in which D is independent of C; both exact and approximate solutions for this relation agree each other within the magnitude of scale herein used.

Figure 7 compares the exact and approximate sorption curves. It is seen that the agreement is best over the others treated above. In fact, within the magnitude of scale herein used, no deviation is detectable between the two curves over the whole time-scale plotted.

B. The case in which D is dependent linearly on concentration

The simplest type of concentration dependence of D is such that in which D changes linearly with C:

$$D(C) = D(0)(1+\lambda C), \tag{90}$$

where $D(0)$ is the value of D at the limit of zero concentration, and λ is a parameter. Recent work on diffusion of low molecular weight substances into high polymeric solids or of macromolecules in dilute solutions has indicated this type of D-C relationship to appear often in actual systems or to be employed as a useful approximation to more complicated concentration dependences. Besides such a practical interest, this D-C relationship has been used by many theoretical workers as a first example with which to test the accuracy of approximate methods of solution worked out by respective authors. Thus, Crank and Henry[4] applied a numerical method, and Osida and Ichikawa[5] and later Mabuchi[6] used somewhat different numerical methods. Osida[7] also worked out a simple method of solving graphically non-linear diffusion problems (not always restricted to one dimension), and applied it to a diffusion coefficient dependent linearly on concentration. In what follows, our approximate solution as derived by the method of moments will be compared with the numerical results of Osida and Ichikawa and with the graphical ones of Osida.

When $D(C)$ is given in the form of equation (90), $F(\psi)$ takes the form:

$$F(\psi) = 1+\sigma\psi \tag{91}$$

with

$$\sigma = \lambda C_0. \tag{92}$$

For convenience, the parameter λ (or σ) is assumed to be positive throughout the consideration below.

First, the solution applicable for $\tau < \tau_*$ is derived. Since, in the present case, $G(1) = 1+\sigma/2$, equation (27) becomes

$$720(1+\sigma)\left(1+\frac{\sigma}{2}\right)\beta^2-(78+93\sigma)\beta+\frac{3}{2} = 0. \tag{93}$$

It can be shown that, if $\sigma > 0$ as has been assumed above, this equation has two positive roots, and that the root fitting our requirement is the larger one, i.e.,

$$\beta=\frac{1}{144(1+\sigma)\left(1+\frac{\sigma}{2}\right)}\left\{(78+93\sigma)+\left[(78+93\sigma)^2-4320(1+\sigma)\left(1+\frac{\sigma}{2}\right)\right]^{\frac{1}{2}}\right\}; \tag{94}$$

this reduces to a value of 1/12 when $\sigma \to 0$, as expected. Either in Osida's work or in Mabuchi' one referred to above, only the special case in which $\sigma = 1$ was treated in practice, and so we shall for the moment confine our consideration to this special case. The cases of larger values of σ will be discussed in section 4 in connection with diffusion in a semi-infinite medium.

Now, with $\sigma = 1$ equation (93) yields

$$\beta\,(=\tau_*) = 0.068340. \tag{95}$$

Consequently, the required expressions for ψ become

$$\psi(z,\ \tau) = 1.57530\left[0.26142\left(\frac{z-1}{\sqrt{\tau}}\right)+1\right]^2 - 0.57530\left[0.26142\left(\frac{z-1}{\sqrt{\tau}}\right)+1\right]^3 \tag{96}$$

$$(1-0.26142\sqrt{\tau} \leqq z \leqq 1),$$

$$\psi(z,\ \tau) = 0 \qquad (0 \leqq z \leqq 1-0.26142\sqrt{\tau}). \tag{97}$$

Figure 8 shows a comparison of the ψ-z curve computed at $\tau = \tau_* = 0.068340$ from equation (96) with the corresponding curve obtained by the graphical method of Osida. A fairly good agreement is observed between the two solutions, except

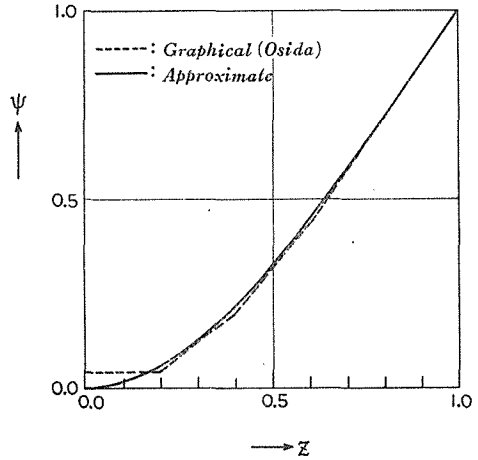

Fig. 8. Concentration distributions at $\tau = 0.068340$ calculated from the present approximate solution and Osida's graphical method for the case in which $D=D(0)(1+\psi)$.

in the neighborhood of the center of the sheet, where both the present and graphical solutions may admittedly involve a considerable error.

Next, we consider the solution in the interval of time after the concentration front has reached the center of the sheet. For the case concerned here the forms of $r(\varphi)$ and $q(\varphi)$ become, respectively, as follows:

$$r(\varphi) = \frac{26}{21} - \frac{5\sigma}{21(1+\sigma)}\varphi,$$

$$q(\varphi) = \varphi - \frac{\sigma}{2(1+\sigma)}\varphi^2.$$

Thus, equation (43) takes the form:

$$\Psi\frac{d\Psi}{d\varphi} = \frac{49}{5}\left\{\left[\frac{26}{21} - \frac{5\sigma\varphi}{21(1+\sigma)}\right]\Psi - \varphi + \frac{\sigma}{2(1+\sigma)}\varphi^2\right\}, \tag{98}$$

which, when $\sigma = 1$, reduces to

$$\Psi \frac{d\Psi}{d\varphi} = \frac{49}{5}\left\{\left(\frac{26}{21} - \frac{5}{42}\varphi\right)\Psi - \left(1 - \frac{\varphi}{4}\right)\varphi\right\}. \tag{99}$$

The corresponding initial condition for $\Psi(\varphi)$ is given by

$$\Psi(1) = 0.42028. \tag{100}$$

It is required to obtain a solution of equation (99) subject to this initial condition in the range $0 < \varphi \leqq 1$. The solution was evaluated numerically with the aid of Runge's method combined with Levy's method.* The result is shown graphically in Figure 9. It is noted from the figure that Ψ converges to zero as φ approaches

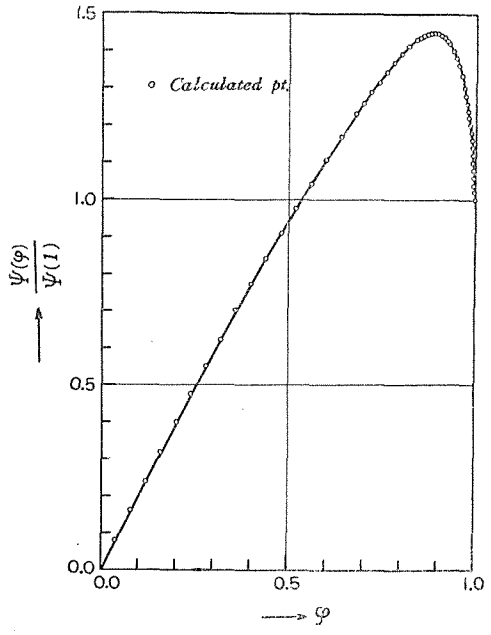

Fig. 9. Integral curve for equation (99).

zero. This behavior is expected if we consider that uniform concentration in the sheet must theoretically be attained after infinite time. In general, a point (0, 0) on the Ψ-φ plane is shown to be an "invariant singular point" such that all the integral curves of equation (43) pass through it, irrespective of the values assigned to the integration constant (hence the values of Ψ (1)). Once the Ψ-φ curve is obtained in this way, the other necessary relations can be derived following the general procedure given in section 2. In Figure 10 the resultant (ψ_e)-τ curve is plotted by solid line, where the corresponding curves obtained respectively by

* Grateful acknowledgment is made for the helpful assistance of Mr. T. Maki in this calculation.

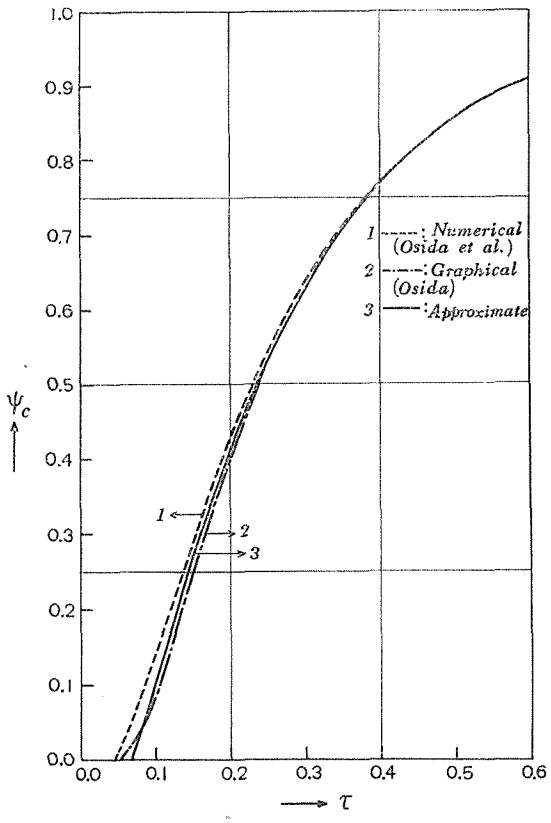

Fig. 10. Comparison of the concentration at the center of the sheet for the case where $D=D(0)\ (1+\phi)$.

means of a graphical and a numerical method are plotted for comparison. Agreement of the three curves is satisfactory, except for a region of τ smaller than about 0.15. It may be recognized that our solution is closer to the graphical solution rather than to the numerical one.

Crank and Henry[4], using the method developed by Crank and Nicolson[8], integrated numerically the diffusion equation relating to a plane sheet with $a=2.5$, 4.8, 7.5 and 10. However, since in their paper only the sorption-time curves are given, it is impossible to compare our solution with theirs with respect to the concentration distribution curve. It is doubtful, however, whether our approximate method of solution is effective for such strongly concentration-dependent diffusion coefficients. This problem is examined in the following section in connection with diffusion into a semi-infinite medium.

Summarizing all the results obtained, it may be stated that, at least so far as the cases in which concentration dependence of D is relatively weak are concerned, the method of moments proviedes solutions of sufficient approximation for problems of diffusion relating to a plane sheet.

4. DIFFUSION INTO A SEMI-INFINITE MEDIUM

The mathematical treatment of problems on diffusion into a semi-infinite medium is simpler than that in the case of a plane sheet. The consideration concerning a semi-infinite medium, however, is largely significant in practice, because the behavior in the early stages of diffusion into a plane sheet may be inspected with a sufficient accuracy from the diffusional behavior in a semi-infinite sheet subject to identical initial and surface conditions.

If we define new dimensionless space and time variables, z and τ, by

$$z=x/L, \quad \tau=tD(0)/L^2$$

using an appropriate unit of length L, and retain the other dimensionless variables as before, the problem to be solved in relation to a semi-infinite medium may be formulated as follows:

$$\frac{\partial\psi}{\partial\tau}=\frac{\partial}{\partial z}\left(F(\psi)\frac{\partial\psi}{\partial z}\right) \quad (0<z<\infty,\ \tau>0), \tag{101}$$

$$\psi(z,\ 0)=0 \quad (0<z<\infty), \tag{102}$$

$$\psi(0,\ \tau)=1 \quad (\tau>0), \tag{103}$$

where the condition of a constant surface cencentration has again been assumed, together with the initial condition that the medium is initially free of diffusing substance. It is also noted that the coordinate origin is here taken on the surface of the medium. As is well known, solutions of equation (101) subject to the conditions (102) and (103) can be represented in terms of a single variable, $z/2\tau^{1/2}$. For example, for a constant diffusion coefficient the solution is given by

$$\psi=1-\mathrm{erf}\,(z/2\tau^{1/2}), \tag{104}$$

where erf denotes the error function.

Crank and Henry[3] solved numerically the above system of equations for a number of diffusion coefficients varying in different ways and in different amounts with concentration, and, with those results, clarified how the concentration distance curve i.e., $\psi-z/2\tau^{1/2}$ curve, is influenced according to the shape and extent of concentration dependence of D. In what follows, we shall hope to check the accuracy and reliability of our approximate method based on some of their results.

The application of the method of moments to the case of a semi-infinite medium can be made in entirely the same way as that employed in the case of a plane sheet for the interval of time before the concentration ceases to be regarded as effectively zero at the center of the sheet. The resultant expression for ψ is given by

$$\psi(z,\ \tau)=\left(\alpha'\beta'-\frac{3}{2}\right)\left(\sqrt{\beta'}\,\frac{z}{\sqrt{\tau}}-1\right)^2+$$

$$+\left(\alpha'\beta'-\frac{5}{2}\right)\left(\sqrt{\beta'}\,\frac{z}{\sqrt{\tau}}-1\right)^3 \quad \left(0\leqq z\leqq\sqrt{\frac{\tau}{\beta'}}\right), \tag{105}$$

$$\psi(z,\ \tau)=0 \quad \left(\sqrt{\frac{\tau}{\beta'}}\leqq z\leqq\infty\right),$$

where α' is

$$\alpha'=30\,G(1) \tag{106}$$

and β' is the larger (positive) root of

$$24\,\alpha'F(1)\,\beta'^2+[\alpha'-108\,F(1)]\beta'+\frac{3}{2}=0. \tag{107}$$

The fact to be noted here is that the quantity β' no longer posseses the same physical meansing as β in equation (27). We may also note that the ψ equation obtained is composed of a single variable $z/\tau^{1/2}$ only, as should be so. Crank and Henry[3] evaluated numerical solutions of equation (101) with conditions (102) and (103) for three types of concentration-dependent diffusion coefficient which are, in the nomenclature of the present paper, written as follows:

$$F(\psi)=1+\sigma\psi, \tag{108}$$

$$F(\psi)=e^{\sigma\psi}, \tag{109}$$

$$F(\psi)=1+50\log(1+\sigma\psi), \tag{110}$$

where σ is a parameter. In what follows, the first two cases are chosen for the comparsion of our approximate solutions with Crank and Henry's numerical solutions.

A. The case in which D is dependent linearly on C

Since Crank and Henry's solutions have been evaluated for as large σ values

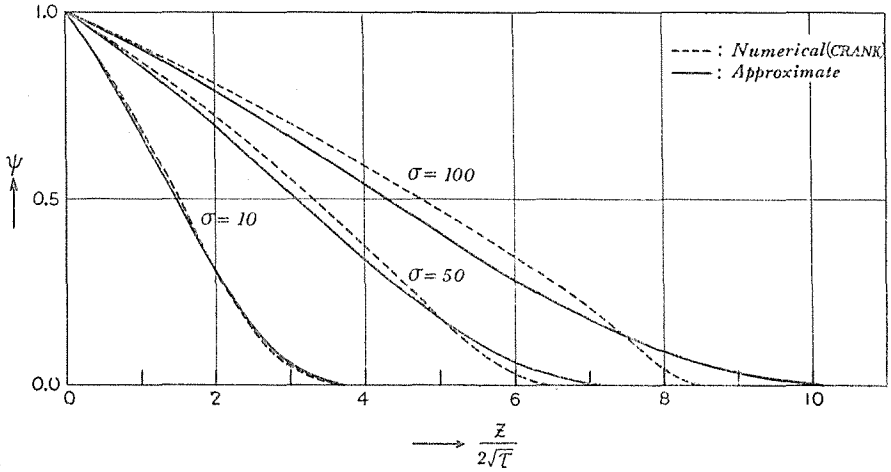

Fig. 11. Concentration distributions in a semi-infinite medium for the case in which $D=D(0)(1+\sigma\psi)$.

as 10, 50, 100, and 200, it is of considerable interest to compare our solutions with theirs for the purpose of understanding the limits of applicability of the method of moments to concentration-dependent diffusions. Figure 11 shows how the present solutions approximate the numerical solutions in the case of a diffusion coefficient dependent linearly on concentration. For $\sigma=10$ our solution gives an approximation of a sufficient degree, and even for as large a σ value as 50 there is observed an approximation satisfactory enough from the practical point of view. However, for $\sigma=100$ there is a great discrepancy which renders our approximate solution worthless. Nevertheless, considering the facility of calculating the $\psi-z/2\tau^{1/2}$ curves by means of the present method, it may be regarded as rather striking that our simple solution can be applied with this degree of accuracy to the case of as large a σ value as 50. At least, for practical purposes, therefore, the present method of solution proves to be effective enough for inspecting the relative behavior of this type of concentration-dependent diffusion in a semi-infinite medium, even when the degree of concentration dependence is remarkably large.

B. The case in which D is dependent exponentially on C

Figure 12 shows the concentration-distance curves when σ is 3.474, which corresponds to $G(1)$ (or D_1 in Crank and Henry's paper[3])$=9.0$. It is seen that our

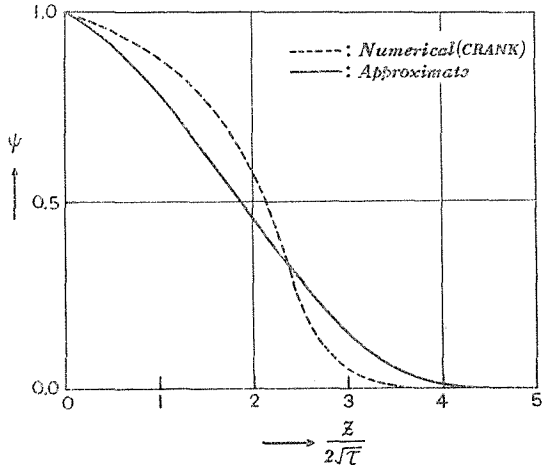

Fig. 12. Concentration distribution in a semi-infinite medium for the case in which $D=D(0)\exp(3.474\ \psi)$.

approximate solution is appreciably deviated from the numerically evaluated solution. Despite that with this value of σ the diffusion coefficient increases only by a factor of 32.266 over the concentration range, the degree of approximation of our solution for this $D-C$ relationship is far worse than that for the linear $D-C$ relationship with $\sigma=50$. Specifically, our solution cannot demonstrate a markedly S-shaped concentration-distance curve that the numerical solution yields. The

reason for such a marked disagreement is probably due to the fact that the way in which D varies with C is different both in the linear $D-C$ relationship and the exponential $D-C$ relationship. It may thus be concluded that the degree of approximation of the present method is very sensitive to the way in which D is dependent on concentration.

Finally, we may remark that, despite a great disagreement in the concentration-distance curve, the areas which the two curves in Figure 12 enclose with the horizontal axis are not so different in size. This indicates that the absorption-time curves computed from these two curves are not so deviated from one another. It may be expected, therefore, that, so far as the sorption-time curve is concernd, approximate solutions by the method of moments will yield results which are comparatively correct and hence satisfactory for most practical purposes, even for such strongly concentration-dependent diffusion coefficients as render the present method inapplicable. Here a possibility is suggested that an approximate method to determine the concentration dependence of D from experimental sorption data may be obtained on the basis of the method of moments. In fact, such a method was derived and applied with success to some acual systems[9].

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REFERENCES

(1) Yamada, H., *Repts. Research Institute for Fluid Eng., Kyushu Univ.* **3** (3), 29 (1947).
(2) Fujita, H., *Memoirs Coll. Agr., Kyoto Univ.* No. **59**, 31 (1951).
(4) Crank, J., and Henry, M. E., *Trans. Faraday Soc.* **45**, 636 (1949).
(5) Osida, I., and Ichikawa, M., *Rebts. Fac. Eng., Nagoya Univ.* **3** (3), 121 (1950).
(6) Mabuchi, I., *Repts. Fac. Eng., Nagoya Univ.* **4** (1), 63 (1951).
(7) Osida, I. *J. Phys. Soc. Japan* **3**, 223 (1948).
(8) Crank, J., and Nicolson, P., *Proc. Cambridge Phil. Soc.* **43**, 50 (1947).
(9) Fujita, H., and Kishimoto, A., *Textile Research J.* **22**, 94 (1952); **23**, 59 (1953).